

Simulation and modeling of hydrogen production from glucose biomass model compound via hydrothermal gasification

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ABSTRACT

Glucose is a 6-carbon carbohydrate compound present in plants and the ingredient for hemicellulose which makes up 30% of plants' total mass. The current study uses glucose as reactant and evaluates hydrogen generation at different temperatures and different amounts of input flow of glucose – water mixture. Hydrothermal gasification method is used for hydrogen generation in an open system with controlled volume with temperature changing in the range of 375 to 1000°C, water intake flow of 800 kg/h and biomass intake flow of 2000 kg/h.

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1. Introduction

Use of renewable energies is one of the important new strategies in energy industry and can play an important role in energy security and controlling climate change. The use of fossil fuels involves numerous problems and environmental damage. Consequently, various studies and a large amount of investment has attempted to produce new, renewable energy sources [1]. Widespread use of fossil fuels such as oil, coal, and natural gas has led to climate change and environmental problems which has motivated many researchers to search for replacement energy sources. Among these studies, hydrogen-

based technologies have gained increased attention as a substitute for fossil fuels due to hydrogen's high energy output and higher compressibility [2]. However, hydrogen is not produced in natural processes and can't be found in its pure form [2]. Since hydrogen-based fuels have zero carbon content, even hydrogen produced using fossil fuels can be considered a green energy source and can lead to a leap toward carbon-free societies and use of renewable energies [3]. Agricultural wastes are a source of lignocellulose compounds and along with other uses as livestock feed and in polymer industries [4] have been utilized to produce the second generation of biodiesels. Presently, around 10% of the energy worldwide is produced using biomass [5]. Lignocellulose is a biomass with highest frequency

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in nonedible materials which is often found in agricultural remains. This type of biomass includes lignin, cellulose and hemicellulose which are degradable and can be processed using new technologies [6, 7]. Among products formed from biomass, hydrogen has gained increased attention as a key energy carrier with multiple applications and environmentally friendly nature [8, 9]. Hydrogen has the highest energy concentration among different products of biomass processing, creating a valuable fuel with Lower Heating Value (LHV¹) of 122 kJ/kg [10]. Hydrogen also has clean combustion with zero pollution and only water as the product and can be used in fuel cells to produce electricity [11]. Hy-

drogen production methods are shown in Figure (1) [12].

Currently, the majority of hydrogen is produced by cracking of fossil fuels. Nevertheless, hydrogen produced from renewable sources is a stable and suitable source for attaining energy stability and security [13]. Under supercritical conditions, water has a low density which supports free radical reactions and is a suitable medium for formation of methane (CH₄) and hydrogen (H₂) [14]. Gasification in supercritical water (T>374°C and P>22.1 MPa) is a novel processing method for lignocellulose which is used to produce gas products such as CO, CO₂, H₂ and CH₄ [15]. This method has several advantages over normal gasification

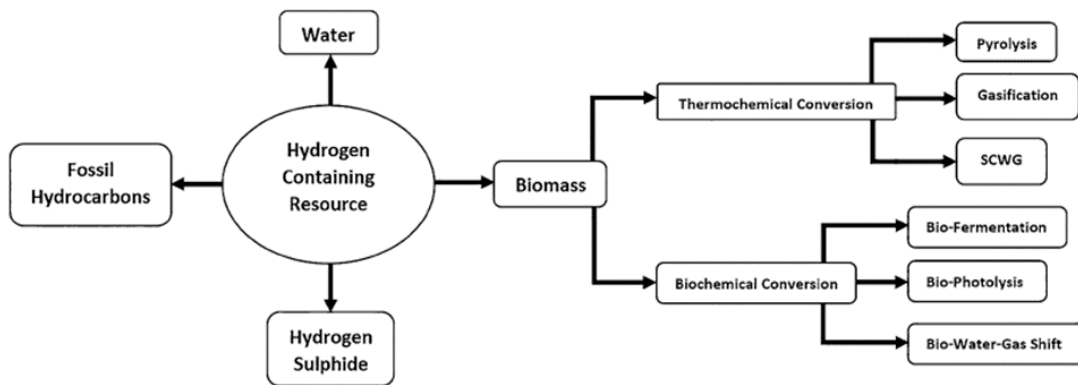


Fig. 1. Process of producing hydrogen from biomass [5]¹

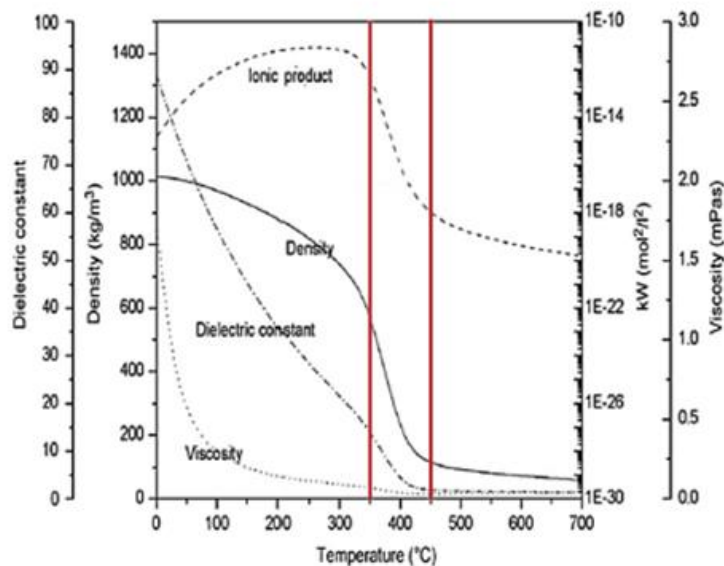


Fig. 2. Changes in water's properties with temperature at pressure of 250 bar [18]

1. Lower Heating Value

technologies which include the possibility of removing drying step from biomass processing and using wet biomass which can lead to significant advantages [16]. Moreover, supercritical water has low density and constant dielectric constant which turns it from a polar to a nonpolar solvent, capable of dissolving organic compounds [17]. As can be seen in Figure 2, at the pressure of 250 bar and by increasing temperature from 350 to 450°C, a significant decrease is observed in density, ionic products and dielectric constant of water which along with free radical mechanisms means that supercritical water is a unique solvent for organic compounds [13].

Under these supercritical conditions, water can easily hydrolyze natural polymers including biomass containing cellulose, hemicellulose and lignin and linear cellulose polymers made from C₅ and C₆ compounds which are the main sources of gasification reaction [6, 19].

The effects of CO₂ produced from gasification process of biomass is small because CO₂ is stabilized using photosynthesis. For instance, one study reports that gasification of biomass vapors along with CO₂ adsorption is a promising method for producing renewable hydrogen [20]. Other processes have also been used for turning biomass into useful fuel products including pyrolysis and gasification of wood in plasma arc [21]. In one study, a plasma torch was created using DC arc and a mixture of argon and water flow. Solar energy has also been used for thermochemical decomposition of biomass and producing various products [21].

When using Gibbs equilibrium reactor design approach, one of the main assumptions used by various studies is that gasification reactions don't quickly reach an equilibrium state [22]. Solar energy is an energy source with alternating nature. This means that combining solar energy with another source such as biomass can improve the general energy production performance. This method however, does not fix the problem of limited supply of biomass which is seasonal and only available at certain times [23, 24]. In addition, maximum solar thermal power depends on the plants and is limited to a certain range [25]. Solar thermal hybridization and biomass combustion are two complementary methods. Both of these processes are seasonal which pose some problems but suitable methods can be employed to store the energy produced [26]. Solar rays are usable by solar panels and biomass can be used as a complimentary fuel source for reaching opera-

ble and stable energy production. Due to their operational flexibility, hydride systems have a promising future. Studies regarding development of solar, wind and other renewable energies often combine them with other common energy sources in order to create a more reliable and predictable energy output [27]. Financial comparison between hydride wind-solar power plants and biomass energy has shown that biomass is a more feasible method [28].

The goal of this study is to investigate hydrogen generation using supercritical water gasification (SCWG¹) of biomass (glucose) at different temperatures of a Gibbs reactor (300, 500, 750 and 1000°) with biomass and water intake flows of 2000 and 800 kg/h, respectively and evaluate the amount of hydrogen produced. The important and novel part of the current study is that the amount of hydrogen produced has not been previously investigated at temperatures higher than 750°C and water – biomass mixture intake of 2800 kg/h (with biomass to water ratio higher than one). Furthermore, each of the products including hydrogen, CO₂ and methane and their production and behavior in temperatures between 0 – 300 and 0 – 1000°C were separately investigated.

In the current study, a thermodynamic model was used for analysis. Products were produced using gasification and the effects of different parameters such as pressure, reactor temperature and water intake of the system were investigated. Gasification under supercritical water conditions has several unique characteristics. There are two different types of equilibriums used in modeling which include stoichiometric and nonstoichiometric equilibriums. The stoichiometric method requires a reference reaction to support all other reactions employed in the modeling. The current study uses gasification reaction as the reference reaction [29]. The chemical formula of biomass can be shown as CH_xO_yN_z in which x, y and z are mole fractions of hydrogen to carbon, oxygen to carbon and nitrogen to carbon, respectively.

The current study uses gasification in supercritical water medium which is one of the most promising methods for producing a hydrogen-rich gas from biomass. This technology has several advantages over thermochemical method. This method can use wet biomass and can synthesize a hydrogen-rich gas with better yield and performance. Water reaches supercritical conditions at temperature of 374°C and pressure of 22.1MPa [30]. Water in SCWG acts in a dual

1. Supercritical water gasification of biomass

role as reactant and reaction solvent. The unique characteristics of supercritical water as a solvent allows it to dissolve a large portion of biomass, creating a homogenous solution. The mixture of water – gas (H₂O and CO) reacts to produce hydrogen and carbon dioxide and is simultaneously methanized, producing CH₄ [31]. The current study investigated hydrogen production at different temperatures below and above supercritical temperature. In this study, the effect of temperature on the production of hydrogen, carbon dioxide and methane in the hydrothermal reaction of water with biomass (glucose) was investigated. With the help of the Aspen Plus software, product behaviors at 375 and 1000 °C were considered.

2. Materials and Methods

As can be seen in Figure (3), first water and biomass were mixed and placed inside a heat exchanger. After increasing the mixture's temperature, the mixture was placed inside the reactor which is analyzed by minimizing Gibbs' free energy. The mixture is again heated in the reactor and after reacting, it enters another heat exchanger to reduce its temperature before reaching a pressure valve. The pressure valve reduces the products' pressure which then enters a separator. This method is used for simultaneous heating and reaction.

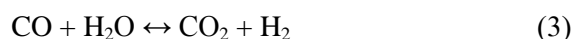
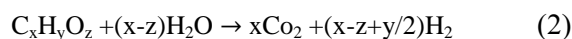
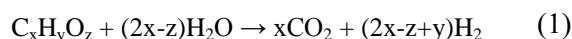
Use of SCWG in hydrogen generation is novel and applicable. This process is one of the most practical methods for renewable energy which can be used at an industrial scale. Currently, SCWG is a developing method which is being investigated in experimental laboratory pilot plants. The method proposed in the current study can be used as a novel system for producing hydrogen using SCWG.

This study first investigates gasification process in reactor, chemical reactions and the effects

of supercritical water temperature and reactor feed intake on the reaction. Then hydrogen production is simulated at different temperatures in ASPEN PLUS software. The schematic of simulation process is shown in Fig.3.

2.2. Reactions

In order to have a clearer understanding of the gasification process of biomass and its products, it is necessary to clarify the chemical reactions occurring in the mixture before analyzing the process. Water reforming in supercritical conditions is used in this work. Water gasification reaction, steam reforming reaction and gas – water reaction are shown in equations (1), (2) and (3), respectively.



Where x and y are H/C and O/C mole fractions in biomass and z is the coefficient of oxygen in equation (2). These reactions are explained in detail in the study by Rashidi Tavasoli [32]. During hydrogen generation in supercritical water medium, along with reactions (1) to (3), reactions (4) and (5) also occur. Reaction (4) shows the gasification chemical reaction of biomass in supercritical water and reaction (5) is the pyrolysis process and reaction (6) shows methanization reaction.

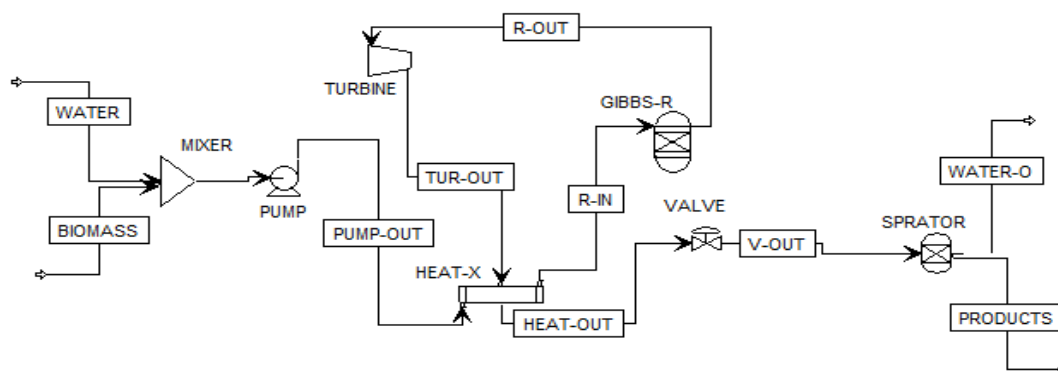
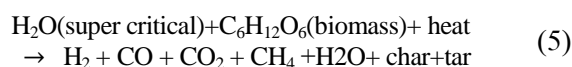
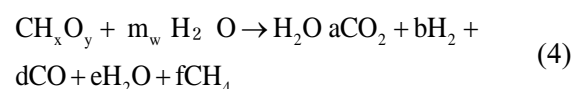
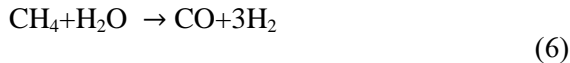


Fig. 3. Schematic of simulation process in ASPEN PLUS software



There are numerous reactions occurring simultaneously in the reactor but the main reactions are reactions (1) to (5), with each being defined and analyzed based on physical reaction conditions, biomass composition and their products. Reactions (1), (2), and (3) are reactions in biomass in the presence of water which result in hydrogen production while reactions (4), (5), and (6) occur at different temperatures and conditions. Reactions (4) and (5) occur in supercritical water and different temperatures. Reactor heating rate and changes in Gibbs' free energy in the reactor are calculated using equations (7) and (8) in which q_h is the heat exchanged in unit of mass, m is mass flow of the feed, ΔH is the changes in enthalpy and ΔS is changes in entropy.

$$\dot{Q} = \dot{m}q_h \quad (7)$$

$$\Delta G = \Delta H - T \Delta S \quad (8)$$

Pump follows equation (9) while heat exchangers follow equations (10) and (11) in which P_0 is the output power of the pump, ΔP is the pressure difference between input and output of the pump, Q is fluid flow rate, q_h and q_c are exchanged heat of hot and cold fluids, m_h and m_c are mass flow of hot and cold fluids, ΔT_h and ΔT_c are the temperature difference between input and output of hot and cold fluids and C_h and C_c are specific heat of hot and cold fluids.

$$P_0 = \Delta P \times Q \quad (9)$$

$$q_{h=\Delta T_h m_h C_h} \quad (10)$$

$$q_{c=\Delta T_c m_c C_c} \quad (11)$$

Since the system is assumed to be open with controlled volume and the changes over time are considered to be negligible (stable system), with negligible potential and kinetic energies, equation (12) shows general first law of thermodynamic for open system and controlled volume with equation (13) showing the solved equation based on these assumptions.

$$\frac{dE_{CV}}{dt} = \dot{Q}_{CV} - \dot{W}_{CV} + \sum \dot{m}_i (h_i + V_i^2 + gZ_i) - \sum \dot{m}_e (h_e + V_e^2 + gZ_e) \quad (12)$$

$$\dot{Q}_{CV} + \dot{m}_i (h_i) = \dot{W}_{CV} + \dot{m}_e (h_e) \quad (13)$$

3. Results and Discussion

3.1. Effect of temperature on products

As earlier mentioned, temperature for hydrogen production was changed between 375 to 1000°C under supercritical water conditions and constant mass flow. The temperatures of 375 and 1000 ° C were chosen for simulation. The properties of the product and the product specification can be mentioned at these two temperatures. As a result, at 375°C, the water has a supercritical property as shown in Fig. 2 and its behavior changes and becomes an organic solvent. The temperature of 1000°C is also the highest temperature, which is optimized for hydrogen production. The growth slope does not suffer from the loss of hydrogen production, and also the effect of coal and bitumen production on the production process of hydrogen is very low, and the production of hydrogen is suitable and growing. Behaviors of hydrogen and other products (CH_4 , CO_2) at different temperatures are shown in Figs 4 to 9.

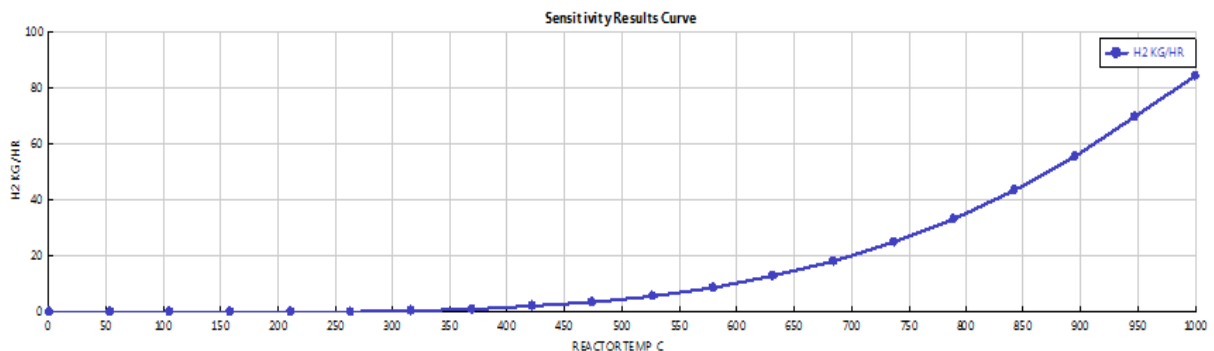


Fig. 4. Hydrogen production at 1000°C and constant mass flow

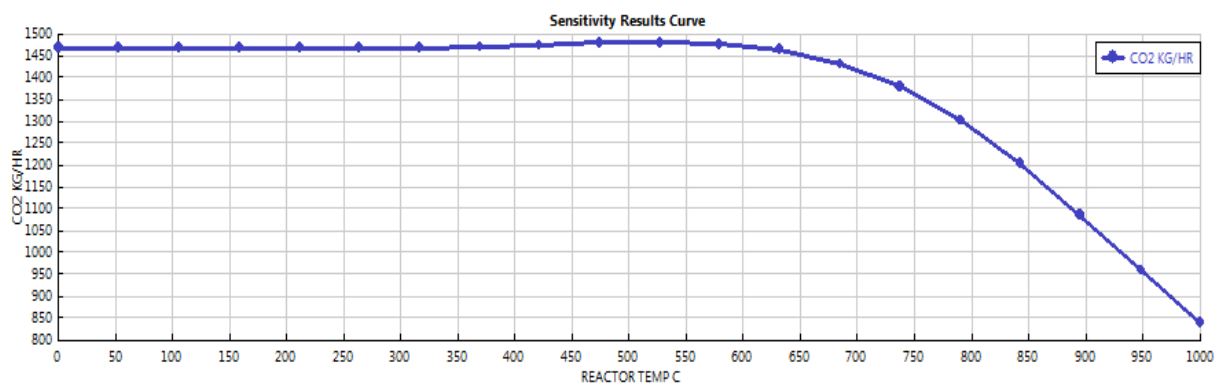


Fig. 5. Carbon dioxide production at 1000°C and constant mass flow

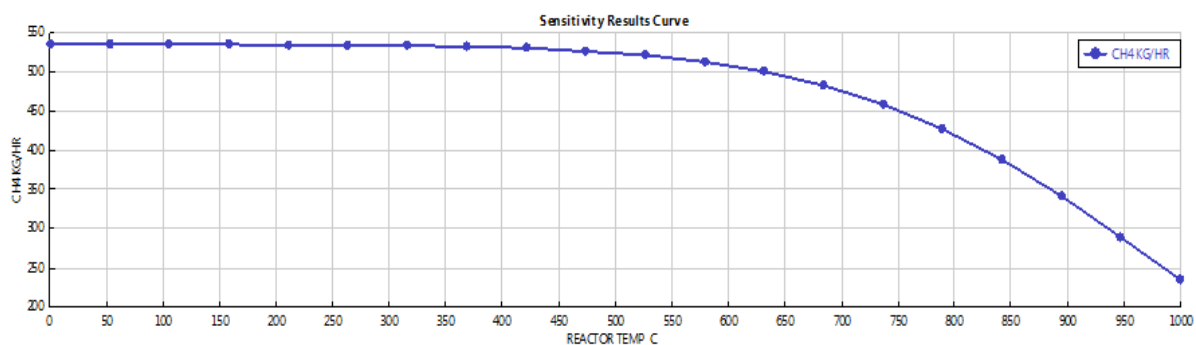


Fig. 6. Methane production at 1000°C and constant mass flow

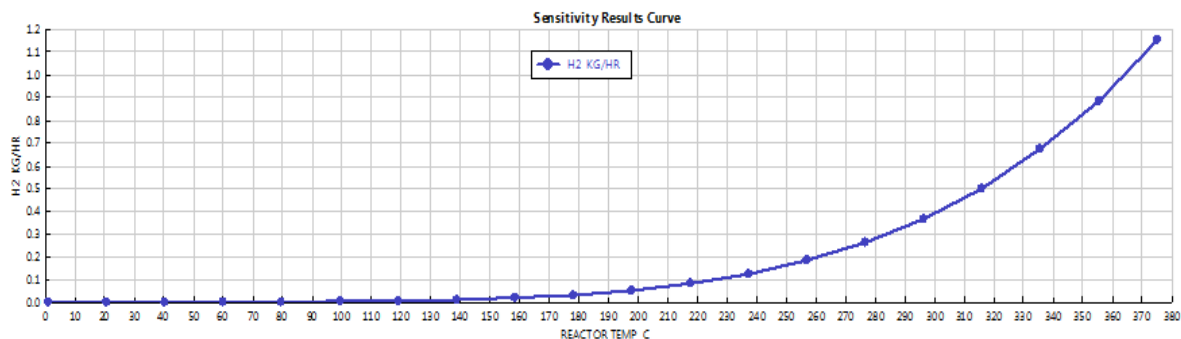


Fig. 7. Hydrogen production at 375 °C and constant mass flow

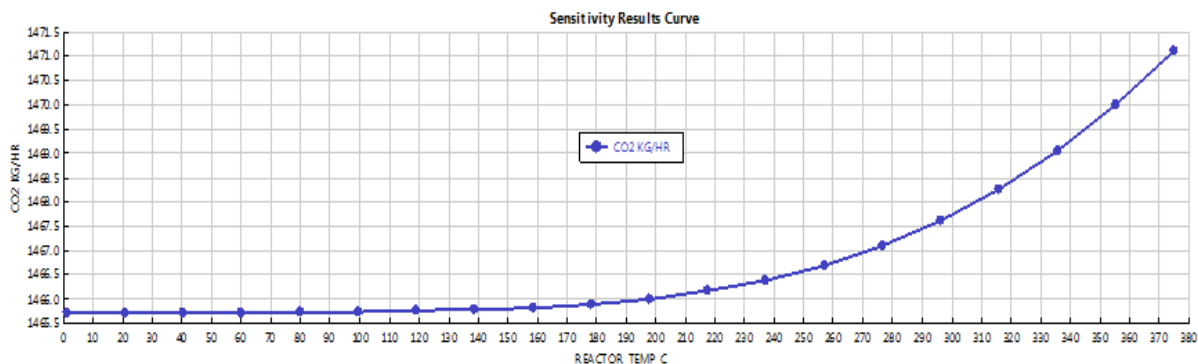


Fig. 8. Carbon dioxide production at 375 °C and constant mass flow

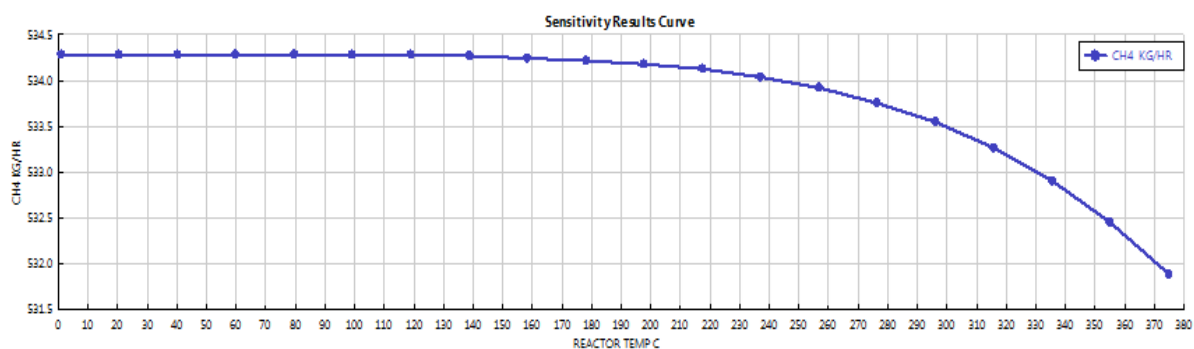


Fig. 9. Methane production at 375 °C and constant mass flow

As can be seen in these figures, at 1000 °C, hydrogen production as an increasing trend increases with increase in temperature. This trend is the opposite for methane and carbon dioxide production. The reason for decreased production of carbon dioxide is that at higher temperatures, due to the formation of coal and tar from biomass, carbon dioxide production decreases based on reaction (5). Methane sometimes acts as reactant for other reactions and therefore always has a decreasing trend. Equation (6) also shows that hydrogen and methane are at different sides of the equation, meaning that increase in hydrogen production leads to decrease in methane.

At 375 °C, hydrogen again shows an increasing trend but the amount of hydrogen produced is small and negligible and is close to zero until 230 °C which is due to endothermic nature of hydrogen generation. This endothermic nature means that hydrogen generation increases with increase in temperature. As earlier mentioned, hydrogen generation occurs in supercritical water and water reaches supercritical conditions at 374 °C. Therefore, the increasing trend in hydrogen generation at temperatures higher than 375 °C is natural due to supercritical water conditions. At temperature of 375 °C, carbon dioxide also shows an increasing trend. Therefore, based on equations (1), (2) and (3), it can be said that hydrogen and carbon dioxide are the main products but at higher temperatures and higher mass flows of biomass, carbon is used up due to higher

amount of tar and coal produced from the biomass, which leads to decreasing trend in carbon dioxide production. As mentioned before, methane always shows a decreasing trend.

4. Conclusion

Biomass gasification modeled in the current study uses glucose as a starting material. Investigating supercritical water conditions under different temperatures (375 to 1000°C) at constant feed mass flow shows that increase in reactor temperature significantly increases the desirable product, which is hydrogen. According to Table 1, hydrogen generation at 1000 °C has increased by 73.2 times compared to hydrogen generation at 375 °C while temperature has only increased by 2.7 times. This is due to supercritical water’s characteristic which acts as a non-polar solvent with constant dielectric constant leading to faster reaction and significant increase in products. This also shows that hydrogen generation is an endothermic process and increase in temperature significantly affects its progress. Table 1 shows the amount of hydrogen, carbon dioxide and methane produced at 375 and 1000 °C.

Based on these results, hydrogen generation at 1000 °C is significantly higher than hydrogen generation at 375 °C while carbon dioxide and methane production has decreased. This shows an opposite trend for hydrogen, CO₂ and CH₄ generation.

Table 1. Products (H₂, CO₂ and CH₄) produced at 375 and 1000 °C

| Reactor temperature (°C) | H ₂ (kg/h) | CO ₂ (kg/h) | CH ₄ (kg/h) |
|--------------------------|-----------------------|------------------------|------------------------|
| 375 | 1.15 | 1471 | 531 |
| 1000 | 84.27 | 838 | 234.58 |

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